# METHOD OF PRODUCING A GLASS SUBSTRATE FOR A MASK BLANK AND METHOD OF PRODUCING A MASK BLANK

This invention claims priority to prior Japanese application JP 2003-90682, the disclosure of which is incorporated herein by reference.

Background of the Invention:

This invention relates to a method of producing a glass substrate for a mask blank and a method of producing a mask blank and, in particular, to a method of producing a glass substrate for a mask blank for use with light in an ultrashort wavelength range, such as F2 excimer laser (fluorine: having a wavelength of 157 nm) and EUV light (extreme ultra violet: having a wavelength of 13 nm), as an exposure light source and a method of producing a mask blank of the type.

Following the improvement of a ULSI device having a higher density and a higher accuracy in recent years, a glass substrate for a mask blank is required to have a substrate surface of a finer structure. Such tendency towards the finer structure of the substrate surface becomes more and more accelerated year by year. In particular, as an exposure light source of a shorter wavelength is used, the demand for a profile accuracy (flatness) and a quality (defect size) of the substrate surface becomes strict. Thus, the glass substrate for a mask blank is required to have an extremely high flatness and to be free from a microscopic defect.

For example, in case where F2 excimer laser is used as the exposure light source, the glass substrate is required to have a flatness of 0.25 μm or less and a defect size of 0.07 μm or less. In case where EUV light is used as the

exposure light source, the glass substrate is required to have a flatness of 0.05 μm or less and a defect size of 0.05 μm or less.

Upon production of a glass substrate for a mask blank, proposal has already been made of a precision polishing technique intended to reduce a surface roughness (for example, see Japanese Patent Application Publication (JP-A) No. 64-40267 (Reference 1)).

The precision polishing technique described in Reference 1 comprises the steps of polishing the substrate surface by the use of an abrasive primarily comprising cerium oxide and then finish-polishing the substrate surface by the use of colloidal silica. In case where the glass substrate is polished by the above-mentioned technique, use is typically made of a double-sided polishing apparatus of a batch type capable of receiving a plurality of glass substrates and simultaneously polishing opposite surfaces of the glass substrates.

In the precision polishing technique mentioned above, it is theoretically possible to achieve a desired flatness by reducing an average grain size of abrasive grains. Actually, however, under the influence of a mechanical accuracy of various components of the polishing apparatus, including a carrier for holding the glass substrate, a surface table for clamping the glass substrate, and a planetary gear mechanism for moving the carrier, and so on, the flatness of the glass substrate stably obtained is limited to about 0.5 μm.

In view of the above, proposal has recently been made of a leveling method for leveling or flattening the glass substrate by local machining using plasma etching or a gas cluster ion beam (for example, see Japanese Patent Application Publication (JP-A) No. 2002-316835 (Reference 2) and Japanese Patent Application Publication (JP-A) No. H08-293483 (Reference 3)).

The leveling method disclosed in References 2 and 3 comprises the steps of measuring a surface profile (convexity and concavity, peak and valley) of the glass substrate and executing local machining upon a convex portion

under a machining condition (such as the amount of plasma etching or the amount of the gas cluster ion beam) depending upon the degree of convexity of the convex portion so as to flatten the surface of the glass substrate.

In case where the flatness of the surface of the glass substrate is adjusted by the local machining using the plasma etching or the gas cluster ion beam, a roughened surface or a surface defect, such as a flaw and a machining-affected layer (a damaged layer), is formed on the glass substrate after the local machining. Therefore, it is necessary to polish the surface of the glass substrate after the local machining in order to repair the roughened surface or to remove the surface defect.

However, if a surface of a polishing tool, such as a polishing pad, is directly contacted with the surface of the glass substrate during polishing after the local machining, the flatness of the surface of the glass substrate may be deteriorated. Therefore, the polishing time is limited to an extremely short time period. This makes it impossible to sufficiently repair the roughened surface and to sufficiently remove the surface defect.

Summary of the Invention:

It is therefore an object of this invention to provide a method of producing a glass substrate for a mask blank, which includes a polishing step of polishing a surface of the glass substrate subjected to local machining in order to repair a roughened surface resulting from the local machining and to remove a surface defect resulting from the local machining, and which is capable of providing a glass substrate high in flatness and smoothness and free from the surface defect by repairing the roughened surface of the glass substrate and removing the surface defect of the glass substrate during the polishing step while maintaining the flatness of the surface of the glass substrate.

It is another object of this invention to provide a method of producing a mask blank by the use of the above-mentioned glass substrate.

According to this invention, there is provided a method of producing a glass substrate for a mask blank, the method comprising:

a profile measuring step of measuring a convex/concave profile of a surface of the glass substrate for a mask blank;

a flatness control step of controlling a flatness of the surface of the glass substrate to a value not greater than a predetermined reference value by specifying the degree of convexity of a convex portion present on the surface of the glass substrate with reference to a result of measurement obtained in the profile measuring step and executing local machining upon the convex portion under a machining condition depending upon the degree of convexity; and

a non-contact polishing step of polishing, after the flatness control step, the surface of the glass substrate subjected to the local machining by the action of a machining liquid interposed between the surface of the glass substrate and a surface of a polishing tool without direct contact therebetween.

In the above-mentioned method, during the polishing step of polishing the surface of the glass substrate subjected to the local machining for the purpose of repairing a roughened surface resulting from the local machining and removing a surface defect resulting from the local machining, the surface of the glass substrate is polished by non-contact polishing by the action of the machining liquid interposed between the surface of the glass substrate and the surface of the polishing tool without direct contact therebetween. Thus, it is possible to repair the roughened surface of the glass substrate and to remove the surface defect on the surface of the glass substrate while maintaining the flatness of the surface of the glass substrate.

Specifically, the non-contact polishing step may be carried out by float polishing, EEM (Elastic Emission Machining), or hydroplane polishing.

In the method of producing a glass substrate for a mask blank according to this invention, the non-contact polishing step is carried out by float polishing.

In the above-mentioned method, the surface of the glass substrate is polished with an extremely small force by contacting the machining liquid with the surface of the glass substrate while the glass substrate is floated or by making fine powder particles collide with the surface of the glass substrate while the glass substrate is floated. Therefore, it is possible not only to repair the roughened surface resulting from the local machining into an ultrafine surface roughness while maintaining the flatness of the surface of the glass substrate but also to remove a microscopic surface defect (a fine surface defect).

In the method of producing a glass substrate for a mask blank according to this invention, the machining liquid comprises an aqueous solution selected from water, an acidic aqueous solution, and an alkaline aqueous solution, and a mixture of the aqueous solution and at least one kind of fine powder particles selected from colloidal silica, cerium oxide, zirconium oxide, and aluminum oxide.

In the above-mentioned method, a polishing force acting upon the surface of the glass substrate is minimized so as to reliably avoid deterioration in flatness resulting from polishing. If the machining liquid containing the alkaline aqueous solution is used, it is possible not only to improve a polishing rate but also to expose a potential defect, such as a flaw, present on the surface of the glass substrate.

In the method of producing a glass substrate for a mask blank according to this invention, the local machining is carried out by plasma etching or a gas cluster ion beam.

In the above-mentioned method, by controlling the moving rate of the ion beam or the moving rate of a plasma source chamber or housing depending upon the degree of convexity of a convex portion on the surface of the glass substrate, it is possible to properly perform the local machining upon the convex portion on the surface of the glass substrate and to control the flatness to a value

not greater than a predetermined reference value.

Alternatively, an ion beam intensity or a plasma intensity may be controlled depending upon the degree of convexity of a convex portion on the surface of the glass substrate.

In the method of producing a glass substrate for a mask blank according to this invention, the reference value is not greater than 0.25 μm.

In the above-mentioned method, by performing the local machining with the reference value of the flatness being 0.25 μm, the glass substrate for a F2 excimer laser exposure mask blank required to have a flatness of 0.25 μm or less can be obtained.

By performing the local machining with the reference value of the flatness being 0.05 μm, the glass substrate for an EUV mask blank required to have a flatness of 0.05 μm or less can be obtained.

A method of producing a mask blank according to this invention comprises the steps of preparing a glass substrate obtained by the method of producing a glass substrate for a mask blank and forming a thin film as a transferred pattern on the glass substrate.

In the above-mentioned method, the F2 excimer laser exposure mask blank or the EUV mask blank having a desired flatness, free from a surface defect, and having a high quality is obtained.

A method of producing a transfer mask according to this invention comprises the steps of preparing the mask blank obtained by the above-mentioned method and patterning the thin film of the mask blank to form a thin film pattern on the glass substrate.

A method of producing a semiconductor device according to this invention comprises the steps of preparing the transfer mask obtained by the above-mentioned method and transferring the thin film pattern of the transfer mask onto a semiconductor substrate by lithography.

Brief Description of the Drawing:

Fig. 1 is a flow chart for describing a production process of a glass substrate for a mask blank according to this invention;

Fig. 2 is a schematic sectional view of a polishing apparatus used in the production process according to this invention;

Fig. 3 is a schematic sectional view of a float polishing apparatus used in the production process according to this invention;

Fig. 4 is a sectional view of a characteristic part of the float polishing apparatus illustrated in Fig. 3;

Fig. 5 is a schematic sectional view of an EEM apparatus;

Fig. 6A is a sectional view of an EUV reflective mask blank which uses the glass substrate according to this invention;

Fig. 6B is a sectional view of an EUV reflective mask which uses the glass substrate according to this invention; and

Fig. 7 is a view for describing pattern transfer using the reflective mask.

Description of the Preferred Embodiment:

Now, an embodiment of this invention will be described with reference to the drawing.

[Method of producing a glass substrate for a mask blank]

At first referring to Fig. 1, description will be made of a method of producing a glass substrate for a mask blank according to this invention.

Referring to Fig. 1, a production process of the glass substrate for a mask blank in this invention includes a preparing step (P-1) of preparing a glass substrate having a surface subjected to precision polishing, a profile measuring step (P-2) of measuring a convex/concave profile of the surface of the glass substrate, a flatness control step (P-3) of controlling a flatness of the surface of the glass substrate by local machining, and a non-contact polishing step (P-4) of polishing the surface of the glass substrate in a non-contact manner.

<Preparing Step (P-1)>

In the preparing step (P-1), preparation is made of a glass substrate with its one surface or opposite surfaces precision-polished by the use of a polishing apparatus which will later be described.

The glass substrate is not particularly restricted but may be any substrate which is suitably used as a mask blank. For example, use may be made of a quartz glass, a soda lime glass, an aluminosilicate glass, a borosilicate glass, and an alkali-free glass.

In case of a glass substrate for a F2 excimer laser exposure mask blank, use may be made of a quartz glass doped with fluorine so as to suppress absorption of exposure light as small as possible.

In case of a glass substrate for an EUV mask blank, use may be made of a glass material having a low thermal expansion coefficient within a range of $0 \pm 1.0 \times 10^{-7}/°C$, preferably within a range of $0 \pm 0.3 \times 10^{-7}/°C$ in order to suppress distortion of a transferred pattern due to heat during exposure.

In the EUV mask blank, a number of films are formed on the glass substrate. Therefore, use is made of a glass material having a high rigidity and capable of suppressing deformation due to film stress. In particular, a glass material having a high Young's modulus of 65 GPa or more is preferable. For example, use may be made of an amorphous glass, such as a $SiO_2$-$TiO_2$ glass and a quartz glass, and a crystallized glass with β-quartz solid solution deposited therein.

Referring to Fig. 2, a polishing apparatus 10 has a polishing portion of a planetary gear system comprising a lower surface table 11, an upper surface table 12, a sun gear 13, an internal gear 14, a carrier 15, and an abrasive supply member 16. The polishing portion polishes the opposite surfaces of the glass substrate by holding the glass substrate in the carrier 15, clamping the glass substrate between the upper and the lower surface tables 11 and 12 with

polishing pads 11a and 12a attached thereto, respectively, supplying an abrasive in an area between the upper and the lower surface tables 11 and 12, and rotating and revolving the carrier 15. Hereinafter, the structure of the polishing portion will be described in detail.

Each of the lower and the upper surface tables 11 and 12 is a disk member having a ring-shaped horizontal plane. The lower and the upper surface tables 11 and 12 have opposite surfaces to which the polishing pads 11a and 12a are attached. The lower and the upper surface tables 11 and 12 are supported to be rotatable around a vertical shaft A (vertical shaft passing through the center of the polishing portion) and are associated with surface table rotation driving portions (not shown), respectively. Driven by the surface table rotation driving portions, the lower and the upper surface tables 11 and 12 are rotated.

The upper surface table 12 is supported to be movable upward and downward along the vertical shaft A. Driven by an upper surface table up/down driving portion (not shown), the upper surface table 12 is moved upward and downward.

The sun gear 13 is disposed at the center of the polishing portion to be rotatable. Driven by a sun gear rotation driving portion (not shown), the sun gear 30 is rotated around the vertical shaft A.

The internal gear 14 is a ring-shaped gear having a series of teeth on an inner peripheral side and is disposed outside the sun gear 13 to be concentric therewith. The internal gear 14 illustrated in Fig. 2 is fixed to be unrotatable. Alternatively, the internal gear 14 may be rotatable around the vertical shaft A.

The carrier (planetary gear) 15 is a thin-plate disk member having a series of teeth on an outer peripheral side and is provided with one or a plurality of work holding apertures for holding the glass substrate.

The polishing portion generally has a plurality of carriers 15. These carriers 15 are engaged with the sun gear 13 and the internal gear 14 and are

rotated and revolved around the sun gear 13 in accordance with the rotation of the sun gear 13 (and/or the internal gear 14).

Each of the upper and the lower surface tables 12 and 11 has an outer diameter smaller than an inner diameter of the internal gear 14. An actual polishing region is a doughnut-like region between the sun gear 13 and the internal gear 14 and between the upper and the lower surface tables 12 and 11.

The abrasive supply member 16 comprises an abrasive storage 16a for storing the abrasive and a plurality of tubes 16b for supplying the abrasive stored in the abrasive storage 16a to the polishing region between the upper and the lower surface tables 12 and 11.

The abrasive comprises fine abrasive grains dispersed in a liquid. For example, the abrasive grains may be silicon carbide, aluminum oxide, cerium oxide, zirconium oxide, manganese dioxide, and colloidal silica. Depending upon the material and the surface roughness of the glass substrate, the abrasive grains are appropriately selected. The abrasive grains are dispersed in a liquid, such as water, an acidic solution, or an alkaline solution, to be used as the abrasive.

The preparing step (P-1) at least comprises a lapping step of lapping the opposite surfaces of the glass substrate and a precision-polishing step of precision-polishing the opposite surfaces of the glass substrate after subjected to lapping. Thus, stepwise polishing is carried out.

For example, the lapping step is carried out by the use of an abrasive obtained by dispersing cerium oxide as relatively large abrasive grains while the precision-polishing step is carried out by the use of an abrasive obtained by dispersing colloidal silica as relatively small abrasive grains.

<Profile Measuring Step (P2)>

The profile measuring step (P-2) is a step of measuring the convex/concave profile (flatness) of the surface of the glass substrate prepared

in the previous step (P-1).

Preferably, the convex/concave profile is measured by a flatness measurement apparatus or profilometer utilizing optical interference in view of a measuring accuracy. The flatness measurement apparatus carries out measurement by irradiating the surface of the glass substrate with coherent light, which is then reflected as reflected light, and detecting a phase difference of the reflected light corresponding to a height difference on the surface of the glass substrate.

For example, the flatness is defined as a difference between the maximum value and the minimum value of a measured plane of the surface of the glass substrate with respect to a virtual absolute plane (focal plane) calculated from the measured plane by a least square method.

The result of measurement of the convex/concave profile is stored in a recording medium such as a computer. Thereafter, the result of measurement is compared with a predetermined reference value (desired flatness) preliminarily be selected. The difference between the result of measurement and the reference value is calculated, for example, by an arithmetic unit of the computer. The difference is calculated for each predetermined region on the surface of the glass substrate. The predetermined region is determined to be coincident with a machining region in the local machining. Thus, the difference in each predetermined region corresponds to a required removed amount to be removed in the local machining for each machining region.

The above-mentioned calculation may be carried out in either the profile measuring step (P-2) or the flatness control step (P-3).

<Flatness Control Step (P-3)>

The flatness control step (P-3) is a step of specifying the degree of convexity of a convex portion present on the surface of the glass substrate with reference to the result of measurement obtained in the profile measuring step

(P-2) and carrying out local machining upon the convex portion under the machining condition corresponding to the degree of convexity to control the flatness of the surface of the glass substrate to a value not greater than the predetermined reference value.

The local machining is carried out under the machining condition selected for each predetermined region on the surface of the glass substrate. The machining condition is determined with reference to the convex/concave profile of the surface of the glass substrate measured by the flatness measurement apparatus and the difference from the predetermined reference value of the flatness (required removed amount in the local machining).

Depending upon a machining apparatus, parameters of the machining condition are different. At any rate, the parameters are determined so that a greater amount is removed as the degree of convexity of the convex portion is greater. For example, in case where the local machining is carried out by the use of an ion beam or plasma etching, the moving rate of the ion beam or the moving rate of a plasma source chamber is controlled to be slower as the degree of convexity is greater. Alternatively, the ion beam intensity or the plasma intensity may be controlled.

As a local machining method used in the flatness control step (P-3), not only the ion beam machining and the plasma etching mentioned above but also various other methods, such as MRF (MagnetoRheological Finishing) and CMP (Chemical-Mechanical Polishing) may be used.

In the MRF, an object to be machined (glass substrate) is locally polished by bringing abrasive grains contained in a magnetic fluid into contact with the object at a high speed and controlling a holding time of a contacted portion between the abrasive grains and the object.

The CMP comprises the steps of polishing a convex portion of the surface of the object by the use of a small-diameter polishing pad and an

abrasive (containing abrasive grains such as colloidal silica) and by controlling the holding time of a contacted portion between the small-diameter polishing pad and the object (glass substrate).

Among the local machining methods mentioned above, local machining by the ion beam, plasma etching, or the CMP leaves a roughened surface or a machining-affected layer on the surface of the glass substrate. Therefore, non-contact polishing (which will later be described) is particularly effective.

Hereinafter, description will be made of the local machining by plasma etching and the ion beam particularly suitable in the flatness control step (P-3).

The local machining method by the plasma etching comprises the steps of positioning the plasma source chamber above a surface portion to be removed and flowing an etching gas to thereby etch the portion to be removed. By flowing the etching gas, neutral radical species generated in plasma isotropically attack the surface of the glass substrate so that the above-mentioned portion is removed. On the other hand, a remaining portion where the plasma source chamber is not located is not etched by collision of the etching gas because no plasma is produced.

When the plasma source chamber is moved on the glass substrate, the removed amount is adjusted by controlling the moving rate of the plasma source chamber or the plasma intensity in accordance with the required removed amount of the surface of the glass substrate.

The plasma source chamber may have a structure in which the glass substrate is clamped by a pair of electrodes. Plasma is generated between the substrate and the electrodes by a high-frequency wave and the etching gas is supplied to thereby generate radical species. Alternatively, the plasma source chamber may comprise a waveguide tube through which the etching gas flows. Plasma is generated by oscillation of microwave to produce a stream of radical species, which impinges on the surface of the glass substrate.

The etching gas is appropriately selected depending upon the material of the glass substrate. For example, use is made of a gas of halogen compound or a mixed gas containing halogen compound. More specifically, use may be made of tetrafluoromethane, trifluoromethane, hexafluoroethane, octafluoropropane, decafluorobutane, hydrogen fluoride, sulfur hexafluoride, nitrogen trifluoride, carbon tetrachloride, silicon tetrafluoride, trifluorochloromethane, and boron trichloride.

The local machining method by the ion beam (irradiation by the gas cluster ion beam) comprises the steps of preparing a substance, such as oxide, nitride, carbide, a rare gas, having a gaseous phase at normal temperature and normal pressure (room temperature and atmospheric pressure) or a mixed gas thereof (a substance as a mixed gas obtained by mixing the above-mentioned substances at an appropriate ratio), forming a gas cluster of the substance, ionizing the gas cluster by electron irradiation to form the gas cluster ion beam, and irradiating a solid surface (surface of the glass substrate) with the gas cluster ion beam in an irradiated region which may be controlled if necessary.

Generally, the cluster comprises a group of several hundreds of atoms or molecules. Even if an accelerated voltage is 10 kV, irradiation occurs as an ultraslow ion beam having energy not greater than several tens eV per atom or molecule. Therefore, the surface of the glass substrate is machined with extremely low damage.

When the surface of the glass substrate is irradiated by the gas cluster ion beam, the molecules or the atoms forming cluster ions collide with atoms of the surface of the glass substrate in multiple stages to produce reflected molecules or atoms having a lateral or horizontal kinetic component. As a result, selective sputtering occurs at the convex portion on the surface of the glass substrate so as to flatten the surface of the glass substrate. Such flattening phenomenon is also obtained by the effect of preferentially sputtering

selected in order to reduce the surface roughness of the glass substrate. Preferably, the average grain size is not greater than several tens nanometers, more preferably not greater than several nanometers. As the abrasive grains having a small average grain size, use may be made of cerium oxide, silica ($SiO_2$), colloidal silica, zirconium oxide, manganese dioxide, and aluminum oxide. Among others, colloidal silica is preferable in view of the surface smoothness in case where the glass substrate is used.

In the non-contact polishing, the machining liquid may be an aqueous solution selected from water, an acidic aqueous solution, and an alkaline aqueous solution. Alternatively, the machining liquid may be a mixture of the aqueous solution and the above-mentioned fine powder particles.

If the water is used, pure water and ultra pure water are preferable.

As the acidic aqueous solution, use may be made of sulfuric acid, hydrochloric acid, hydrofluoric acid, and fluorosilicic acid. If the acidic aqueous solution is contained in the machining liquid used in the non-contact polishing, the polishing rate is improved. However, depending upon the type of the acid or if the concentration of the acidic aqueous solution is high, the glass substrate may be roughened. Therefore, the type of the acid and the concentration are appropriately selected so as not to roughen the glass substrate.

As the alkaline aqueous solution, use may be made of an aqueous solution of potassium hydroxide or sodium hydroxide. If the alkaline aqueous solution is contained in the machining liquid used in the non-contact polishing, the polishing rate is improved. Further, if a potential microscopic defect (crack, flaw, or the like) is present on the surface of the glass substrate, such potential microscopic defect is exposed. It is therefore possible to reliably detect the microscopic defect in an inspection step subsequently carried out. The alkaline aqueous solution is adjusted within a range such that the abrasive grains contained in the machining liquid are not dissolved. It is preferable to adjust the

those atoms present on the surface or grains and having a weak bond, by the energy concentrated to the surface of the glass substrate.

The generation of the gas cluster itself is already known. That is, the gas cluster can be produced by blowing a gaseous substance in a compressed state into a vacuum apparatus through an expansion nozzle. The gas cluster thus produced can be ionized by irradiation with electrons.

Herein, the gaseous substance may be oxide, such as $CO_2$, CO, $N_2O$, NOx, and CxHyOz, $O_2$, $N_2$, and a rare gas such as Ar and He.

The flatness required to the glass substrate for a mask blank is determined in correspondence to the wavelength of an exposure light source used for the mask blank. Depending upon the required flatness, the reference value for controlling the flatness in the flatness control step (P-3) is determined.

For example, in case of the glass substrate for a F2 excimer laser exposure mask blank, the reference value for controlling the flatness is not greater than 0.25 μm. In case where the glass substrate for an EUV mask blank, the reference value for controlling the flatness is not greater than 0.5 μm. By the use of the reference value, the local machining is carried out.

<Non-Contact Polishing Step (P-4)>

The non-contact polishing step (P-4) is a step of polishing the surface of the glass substrate subjected to the local machining in the flatness control step (P-3) by the action of a machining liquid interposed between the surface of the glass substrate and a surface of a polishing tool without direct contact therebetween.

A non-contact polishing method used in this step is not particularly limited. For example, use may be made of float polishing, EEM, and hydroplane polishing.

As fine powder particles to be contained in the machining liquid used in non-contact polishing, abrasive grains having a small average grain size are

alkaline aqueous solution so that the machining liquid has a pH of 9-12.

Hereinafter, description will be made of the principle of machining by each of the float polishing, the EEM, and the hydroplane polishing.

A polishing plate used in the float polishing has a surface provided with a plurality of grooves for leading the machining liquid and formed into a shape such that a dynamic or kinetic pressure is generated. As the machining liquid, use is made of fine powder particles having an average grain size of several nanometers to several tens nanometers and suspended in a solvent (such as pure water or an alkaline aqueous solution). In the machining liquid, the polishing plate and an object to be machined (glass substrate) are simultaneously rotated in the same direction in the state where a polishing plate axis (main shaft) and a rotation shaft of the object are eccentric from each other at a predetermined distance.

At this time, the object is allowed to freely float up and down and to receive only a rotation torque transmitted thereto. According to a dynamic pressure effect, a small gap is formed between the object and the polishing plate and the object floats up. The fine powder particles passing through the gap collide with a machined surface of the object so that microscopic destruction is repeated. Thus, machining of the object proceeds. Because of the above-mentioned principle, the object can be machined to an ultrafine surface roughness. In addition, machining itself is carried out with a small force so that the machined surface is finished without a machining-affected layer.

In case where the object is a glass substrate, $CeO_2$ (having a ultra high purity) or colloidal silica may be used as the fine powder particles.

The EEM is a non-contact polishing method in which fine powder particles of 0.1 μm or less are contacted with the object in a substantially no load condition. By an interaction (a sort of chemical bond) produced at an interface between the fine powder particles and the object, atoms on the surface of the

object are removed per atom. According to the principle of machining mentioned above, machining characteristics greatly depend upon the affinity between the fine powder particles and the object. In order to efficiently machine the object, the fine powder particles are appropriately selected depending upon the material of the object. For example, in case where the object is a glass substrate, zirconium oxide, aluminum oxide, and colloidal silica may be used as the fine powder particles. In order to improve the machining rate, the fine powder particles are suspended in a solvent causing erosion of the object to obtain the machining liquid, which is contacted with the object.

In the hydroplane polishing, the object is fixed to a disk-shaped plate having a conical outer periphery to face a polishing pad. The outer periphery of the disk-shaped plate is supported by three rollers so that the object is separated from the surface of the polishing pad by about 100 $\mu$m. When an abrasive layer is formed between the polishing pad and the object and a space between the polishing pad and the object is filled with the abrasive, the object and the disk-shaped plate follow the rotation of the polishing pad and machining proceeds.

Next, description will be made of a float polishing apparatus and an EEM apparatus.

Referring to Fig. 3, the float polishing apparatus 20 comprises a rotary table 21, a cylindrical machining tank 22 placed on the rotary table 21 and storing a machining liquid, a main shaft 23 which is a rotation shaft of the rotary table 21, a polishing plate 24 disposed on the rotary table 21 to be eccentric at a predetermined distance with respect to the main shaft 23, a work holder shaft 25 concentric with the polishing plate 24, a work holder 26 faced to the polishing plate 24 and rotatable around the work holder shaft 25, and a machining liquid supply member 27 for supplying the machining tank 22 with the machining liquid containing fine powder particles.

The rotary table 21 is required to have a high rigidity and a resistance against the machining liquid. Therefore, the rotary table 21 is made of a material having the above-mentioned characteristics. Preferably, a stainless steel is used. Further, the rotary table 21 requires a high rotation accuracy and a high vibration absorbability. Therefore, the rotary table 21 is preferably supported by a high-performance bearing such as a hydrostatic oil bearing.

The rotary table 21 is provided with a discharge port (not shown) for discharging the machining liquid supplied from the machining liquid supply member 27. Ahead of the discharge port, a collecting mechanism (not shown) for collecting machining scraps produced by the float polishing is disposed. During machining, the discharge port is kept opened. By controlling the amount of the machining liquid supplied from the machining liquid supply member 27, a liquid level of the machining liquid in the machining tank 22 is maintained.

Driven by a rotation driving member (not shown), the rotary table 21 is rotated around the main shaft 23 at a rotation speed of several tens rpm to several hundreds rpm.

Driven by a rotation driving member (not shown), the work holder 26 is rotated around the work holder shaft 25 at a rotation speed of several tens rpm to several hundreds rpm. The work holder 26 is supported so as to float up and down and receives only a rotation driving torque transmitted thereto. Thus, the work holder 26 is allowed to float up and down during machining. The work holder 26 is rotated in a rotating direction same as that of the rotary table 21.

The object to be machined is held in a manner such that the object is not given a damage such as a flaw. For example, the object is fixed to the work holder 26 by vacuum suction or an adhesive.

The polishing plate 24 has a doughnut-like shape around the main shaft 23 of the rotary table 21 and has a width at least greater than the size of the object. Since the object is rotated around the work holder shaft 25 on the

polishing plate 24, the width of the polishing plate 24 is greater than the diagonal length of the object if the object has a square shape and is greater than the long diagonal length of the object if the object has a rectangular shape.

Referring to Fig. 4, the polishing plate 24 has an upper surface of a non-flat shape or a convex/concave shape. Between a plurality of convex portions 24a, a plurality of grooves 24b for leading the machining liquid are formed. Each of the convex portions 24a has an upper part formed into a tapered shape so as to produce a dynamic pressure upon the object. By an inclination angle of the tapered shape, a floating force (floating distance) of the object is controlled. The inclination angle of the tapered shape is appropriately adjusted within a range of 1° and 20° depending upon the size of the object or the like so that the floating distance of the object is several microns. Herein, the floating distance is a distance between the convex portion 24a of the polishing plate 24 and the object, i.e., a gap in which the machining liquid is present. The width, the depth, and the pitch of the groove 24b controls leading of the machining liquid. The groove 24b has a width appropriately selected between 1 and 5 mm, a depth appropriately selected between 1 and 10 mm, and a pitch appropriately selected between 0.5 and 30 mm.

The polishing plate 24 is made of a material resistant against the machining liquid. For example, a stainless steel, tin, ceramics may be used.

Depending upon a liquid temperature of the machining liquid, the polishing plate 24, the rotary table 21, the work holder 26, and the object may be thermally deformed so that the machining accuracy is affected. Therefore, the machining liquid is accurately controlled in temperature.

For example, the machining liquid comprises a solvent, such as pure water, ultra pure water, an alkali, or an acid, or a mixture of the solvent and fine powder particles contained therein. The concentration of the fine powder particles is within a range of 0.1-40 wt%.

The machining liquid supply member 27 may circulate the machining liquid in the manner such that the machining liquid discharged from the discharge port is supplied again into the machining tank 22 after the machining scraps contained in the machining liquid are removed by a dust collector. Alternatively, the machining liquid supply member 27 may supply a new machining liquid into the machining tank 22 in an amount corresponding to the machining liquid discharged from the discharge port. In the float polishing, the thickness of a machining liquid layer interposed between the polishing plate 24 and the object is an important factor. Therefore, the amount of the machining liquid supplied from the machining liquid supply member 27 is controlled with high accuracy in order to strictly control the amount of the machining liquid in the machining tank 22.

Referring to Fig. 5, the EEM apparatus 30 comprises a machining tank 31 storing a machining liquid, an object holding member 32 for holding an object in the machining tank 31, a rotation shaft 33 extending towards a surface of the object, a rotary member 34 rotatable around the rotation shaft 33 so that the machining liquid (fine powder particles) is preferentially contacted with a specific region on the surface of the object, a moving member 35 for moving the rotary member 34 upward, downward, leftward, rightward with respect to the object, and a machining liquid supply member 36 for supplying the machining liquid containing the fine powder particles into the machining tank 31.

The machining tank 31 is made of a material resistant against the machining liquid. The machining tank 31 is provided with a discharge port 31a for discharging the machining liquid supplied from the machining liquid supply member 36. Ahead of the discharge port 31a, a collecting mechanism (not shown) for collecting machining scraps produced by the EEM is disposed. During machining, the discharge port 31a is kept opened. By controlling the amount of the machining liquid supplied from the machining liquid supply

member 36, a liquid level of the machining liquid in the machining tank 31 is maintained.

The object to be machined is held in a manner such that the object is not given a damage such as a flaw.

The shape of the rotary member 34 is appropriately selected in correspondence to the specific region on the surface of the object as a region which is to be preferentially contacted (reacted) with the machining liquid. In case where the machining liquid is to be preferentially contacted with a relatively narrow region, the rotary member 34 has a spherical shape or a linear shape. In case where the machining liquid is to be preferentially contacted with a relatively large region, the rotary member 34 has a cylindrical shape.

The rotary member 34 is made of a material resistant against the machining liquid and having a low elasticity. If the rotary member 34 has a high elasticity (relatively soft), deformation may occur during rotation and the shape may become unstable so that the machining accuracy is degraded. For example, the rotary member 34 may be made of polyurethane, glass, ceramics.

[Method of Producing a Mask Blank]

Next, description will be made of a method of producing a mask blank according to one embodiment of this invention.

The method of producing a mask blank according to this invention comprises the steps of preparing a glass substrate obtained by the above-mentioned method of producing a glass substrate for a mask blank and forming a thin film as a transferred pattern on the glass substrate.

The mask blank is classified into a transmissive mask blank and a reflective mask blank. In either mask blank, the thin film as the transferred pattern is formed on the glass substrate. A resist film may be formed on the thin film.

The thin film formed on the transmissive mask blank causes optical change in exposure light (light emitted from the exposure light source) used in pattern transfer to a transfer object. For example, the thin film may be a light shielding film (an opaque film) for shielding the exposure light or a phase shift film for changing the phase of the exposure light.

Generally, the light shielding film may be a Cr film, a Cr alloy film selectively containing oxygen, nitrogen, carbon, or fluorine in addition to Cr, a laminated film thereof, a MoSi film, a MoSi alloy film selectively containing oxygen, nitrogen, or carbon in addition to MoSi, and a laminated film thereof.

The phase shift mask may be a $SiO_2$ film having a phase shift function alone, a metal silicide oxide film, a metal silicide nitride film, a metal silicide oxynitride film, a metal silicide oxycarbide film, a metal silicide oxycarbonitride film (metal: transition metal such as Mo, Ti, W, Ta) each of which has a phase shift function and a light shielding function, and a halftone film such as a CrO film, a CrF film, and a SiON film.

The reflective mask blank comprises a glass substrate and a laminated film formed thereon and including a reflective multilayer film (reflective multilayer film) and a light absorber film (absorber layer) as a transferred pattern.

The reflective multilayer film may comprise a Ru/Si periodic multilayer film, a Mo/Be periodic multilayer film, a Mo-compound/Si-compound periodic multilayer film, a Si/Nb periodic multilayer film, a Si/Mo/Ru periodic multilayer film, a Si/Mo/Ru/Mo periodic multilayer film, and a Si/Ru/Mo/Ru periodic multilayer film.

The light absorber film may be made of a material such as Ta, Ta alloy (for example, a material containing Ta and B, a material containing Ta, B, and N), Cr, Cr alloy (for example, a material containing Cr and at least one element selected from nitrogen, oxygen, carbon, and fluorine).

For the transmissive mask blank, g ray (having a wavelength of 436 nm), i ray (having a wavelength of 365 nm), KrF (having a wavelength of 246 nm), ArF (having a wavelength of 193 nm), or F2 (having a wavelength of 157 nm) may be used as the wavelength of the exposure light source. For the reflective mask blank, EUV (having a wavelength of 13 nm) may be used as the wavelength of the exposure light source.

For example, the above-mentioned thin film may be formed by sputtering such as DC sputtering, RF sputtering, ion beam sputtering.

[Examples and Comparative Examples]

Hereinafter, description will be made of examples of this invention in conjunction with a method of producing a glass substrate for an EUV reflective mask blank (hereinafter simply be referred to as a glass substrate) and a method of producing an EUV reflective mask blank. It will readily be understood that this invention is not limited to the following examples.

<Example 1: Float Polishing>

Preparation was made of a glass substrate (having a size of 152.4 mm x 152. 4mm and a thickness of 6.35 mm) which has been polished stepwise by cerium oxide abrasive grains and colloidal silica abrasive grains by the use of the above-mentioned polishing apparatus 10.

The surface profile (flatness) of the glass substrate was measured by a flatness measurement apparatus utilizing optical interference. As a result, the glass substrate had a flatness of 0.2 μm (convex) and a surface roughness of 0.15 nm as a root-mean-square roughness Rq (= RMS). The root-mean-square roughness Rq is also disclosed in United States Patent No. US 6544893 B2.

The result of profile measurement of the surface of the glass substrate was stored in a computer and compared with a reference value of 0.05 μm (convex) as a required flatness for the glass substrate for an EUV mask blank.

The difference (required removed amount) between the measured flatness and the reference value was calculated by the computer.

Next, for every predetermined region (5 mm square) within the plane of the glass substrate, the machining condition for local plasma etching was determined in correspondence to the required removed amount. According to the machining condition thus determined, the profile was adjusted by the local plasma etching so that the flatness of the glass substrate is not greater than the reference value (flatness of 0.05 $\mu$m).

The local plasma etching was carried out by the use of tetrafluoromethane as an etching gas and a plasma source chamber of a high-frequency type having a cylindrical electrode.

After the profile was adjusted by the local plasma etching, the flatness of the surface of the glass substrate was measured. As a result, the flatness was as excellent as 0.05 $\mu$m. The surface roughness Rq of the surface of the glass substrate was equal to about 1 nm. Thus, the surface was roughened as a result of the plasma etching.

The glass substrate was mounted to the float polishing apparatus 20 mentioned above and subjected to non-contact polishing.

The polishing condition in the float polishing was as follows:

Machining liquid (Polishing slurry): pure water + fine powder particles (concentration of 2 wt%)

Fine powder particles: silica ($SiO_2$) having average grain size of about 70 nm

Rotation speed of rotary table: 5-200 rpm

Rotation speed of work holder: 10-300 rpm

Polishing time: 5-30 min

Thereafter, the glass substrate was cleaned by an alkali aqueous solution to obtain the glass substrate for an EUV mask blank.

The flatness and the surface roughness of the glass substrate thus obtained were measured. As a result, the flatness was as excellent as 0.05 μm, i.e., the level before the float polishing was maintained. The surface roughness Rq was 0.09 nm. Thus, the roughened surface of the glass substrate before the float polishing was repaired.

The surface defect of the surface of the glass substrate was inspected by a defect inspection apparatus described in Japanese Patent Application Publication (JP-A) No. H11-242001. The inspection apparatus carries out defect inspection by introducing a laser beam from a chamfered surface of the substrate, confining the laser beam by total reflection, and detecting light scattered by the defect and leaking out from the substrate. As a result of the defect inspection, no flaw having a size exceeding 0.05 μm was found.

Thus, the glass substrate thus obtained satisfied the specification required for a glass substrate for an EUV mask blank.

<Example 2: Machining Liquid for Float Polishing>

A glass substrate was produced in the manner similar to Example 1 except that the float polishing was carried out under the following condition.

Machining liquid (Polishing slurry): alkali aqueous solution (NaOH) + fine powder particles (concentration of 2 wt%), pH: 11

Fine powder particles: colloidal silica having an average grain size of 70 nm

Rotation speed of rotary table: 5-200 rpm

Rotation speed of work holder: 10-300 rpm

Polishing time: 3-25 min

Thereafter, the glass substrate was cleaned by an alkali aqueous solution (NaOH) to obtain the glass substrate for an EUV mask blank.

The flatness and the surface roughness of the glass substrate thus obtained were measured. As a result, the flatness and the surface roughness were substantially same as those of the glass substrate obtained in Example 1. The surface defect of the surface of the glass substrate was inspected by the defect inspection apparatus described in Japanese Patent Application Publication (JP-A) No. H11-242001. As a result, no flaw having a size exceeding 0.05 μm was found. By the use of the alkali aqueous solution as a solvent of the machining liquid, the polishing rate was improved and the polishing time was shortened.

<Example 3: Machining Liquid 2 for Float Polishing>

A glass substrate was produced in the manner similar to Example 1 except that the float polishing was carried out under the following condition.

Machining liquid (Polishing slurry): alkali aqueous solution (NaOH) 5 vol%

Fine powder particles: none

Rotation speed of rotary table: 5-200 rpm

Rotation speed of work holder: 10-300 rpm

Polishing time: 7-45 min

Thereafter, the glass substrate was cleaned by pure water to obtain the glass substrate for an EUV mask blank.

The flatness and the surface roughness of the glass substrate thus obtained were measured. As a result, the flatness and the surface roughness were substantially same as those of the glass substrate obtained in Example 1. The surface defect of the surface of the glass substrate was inspected by the defect inspection apparatus described in Japanese Patent Application Publication (JP-A) No. H11-242001. As a result, no flaw having a size exceeding 0.05 μm was found. By the use of the alkali aqueous solution as a solvent of the machining liquid, the polishing rate was improved and the

polishing time was shortened.

<Example 4: EEM>

A glass substrate was produced in the manner similar to Example 1 except that the EEM was carried out as the non-contact polishing after the flatness was adjusted by the local plasma etching. The EEM was carried out in the following condition.

Machining liquid (Polishing slurry): pure water + fine powder particles (concentration: 3 wt%)

Fine powder particles: zirconium oxide ($ZrO_2$) having an average particle size of about 60 nm

Rotary member: polyurethane roll

Rotation speed of rotary member: 10-300 rpm

Rotation speed of work holder: 10-100 rpm

Polishing time: 5-30 min

Thereafter, the glass substrate was cleaned by an alkali aqueous solution to obtain the glass substrate for an EUV mask blank.

The flatness and the surface roughness of the glass substrate thus obtained were measured. As a result, the flatness was as excellent as 0.05 μm, i.e., the level before the float polishing was maintained. The surface roughness Rq was 0.11 nm. Thus, the roughened surface of the glass substrate before execution of the EEM was repaired. The surface roughness is slightly greater than those in Examples 1 to 3 presumably under the influence of hardness of the fine powder particles.

The surface defect of the surface of the glass substrate was inspected by a defect inspection apparatus described in Japanese Patent Application Publication (JP-A) No. H11-242001. As a result, no flaw having a size exceeding 0.05 μm was found.

Thus, the glass substrate obtained as mentioned above satisfied the specification required for a glass substrate for an EUV mask blank.

<Comparative Example>

A glass substrate was prepared in the manner similar to Example 2 except that, as polishing after the flatness was adjusted by the local plasma etching, one-side polishing was carried out in the following manner. The glass substrate was mounted to a polishing plate faced to a polishing surface table. The glass substrate was rotated and pressed downward against a polishing pad region on the polishing surface table which is rotated. The one-side polishing was carried out in the following condition.

Machining liquid (Polishing slurry): alkali aqueous solution (NaOH) + fine powder particles (concentration of 2 wt%), pH: 11

Fine powder particles: colloidal silica having an average grain size of about 70 nm

Rotation speed of polishing surface table: 1-50 rpm

Rotation speed of polishing plate: 1-50 rpm

Machining pressure: 0.1-10 kPa

Polishing time: 1-10 min

Thereafter, the glass substrate was cleaned by an alkali aqueous solution (NaOH) to obtain the glass substrate for an EUV mask blank.

The flatness and the surface roughness of the glass substrate thus obtained were measured. As a result, the surface roughness Rq was as excellent as 0.15 nm. The flatness was 0.25 μm which was degraded as compared with that before the one-side polishing and that before the flatness was adjusted by the local plasma etching.

The surface defect of the surface of the glass substrate was inspected by the defect inspection apparatus described in Japanese Patent Application

Publication (JP-A) No. H-242001. As a result, a number of flaws exceeding 0.05 μm were found. This is presumably because foreign matters present in the polishing pad damaged the glass substrate during the polishing since the polishing is performed in the state where the glass substrate is contacted with the polishing pad.

As a result, the glass substrate obtained in Comparative Example did not satisfy the specification required for a glass substrate for an EUV mask blank.

<Production of EUV reflective mask blank and EUV reflective mask>

Referring to Figs. 6A and 6B, production of the EUV reflective mask blank and the EUV reflective mask will be described.

On a glass substrate 101 obtained either in each of Examples 1 to 4 or in Comparative Example, 40 periods of Si films and Mo films were laminated by DC magnetron sputtering. It is noted here that a single period of deposition includes a Si film having the thickness of 4.2 nm and a Mo film having the thickness of 2.8 nm. Then, another Si film having the thickness of 11 nm was formed. Thus, a reflective multilayer film 102 was produced. Next, by DC magnetron sputtering, a chromium nitride (CrN) film having the thickness of 30 nm as a buffer layer 103 and a TaBN film having a thickness of 60 nm as an absorber layer 104 were formed on the reflective multilayer film 102. Thus, the EUV reflective mask blank 100 was obtained.

Next, by the use of the EUV reflective mask blank 100, an EUV reflective mask 100a with a 16 Gbit-DRAM pattern having a design rule of 0.07 μm was produced.

At first, an EB resist was applied to the EUV reflective mask blank 100. By EB writing and development, a resist pattern was formed.

Next, using the resist pattern as a mask, the absorber layer 104 was dry-etched using chlorine to form an absorber pattern 104a on the EUV reflective

mask blank 100.

The resist pattern left on the absorber pattern 104a was removed by hot sulfuric acid. Thereafter, the buffer layer 103 was dry-etched following the absorber pattern 104a by the use of a mixed gas of chlorine and oxygen to form a patterned buffer layer 103a. Thus, the EUV reflective mask 100a was obtained.

Next referring to Fig. 7, description will be made of a method of transferring a pattern by EUV light onto a semiconductor substrate with a resist by the use of the EUV reflective mask 100a.

A pattern transfer apparatus 120 illustrated in the figure comprises a laser plasma X-ray source 121, the EUV reflective mask 100a, and a reducing optical system 122. The reducing optical system 122 comprises an X-ray reflection mirror. The pattern reflected by the EUV reflective mask 100a is reduced to about 1/4. Since the wavelength band of 13-14 nm is used as the exposure wavelength, an optical path is preliminarily positioned in vacuum.

In the above-mentioned state, EUV light emitted from the laser plasma X-ray source 121 is incident to the EUV reflective mask 100a. The light reflected by the EUV reflective mask 100a is transferred to the semiconductor substrate 110 with a resist through the reducing optical system 122.

Specifically, the light incident to the EUV reflective mask 100a is absorbed by the absorber layer 104 and is not reflected in an area where the absorber pattern 104a is present. On the other hand, the light incident to a remaining area where the absorber pattern 104a is not present is reflected by the reflective multilayer film 102. Thus, a pattern formed by the reflected light from the EUV reflective mask 100a is transferred through the reducing optical system 122 to a resist layer on the semiconductor substrate 110.

By the use of the EUV reflective mask 100a comprising the glass substrate 101 obtained in each of Examples 1-4 and Comparative Example,

pattern transfer onto the semiconductor substrate was carried out by the pattern transfer method mentioned above. As a result, it was confirmed that the EUV reflective mask 100a in each of Examples 1-4 had an accuracy of 16 nm or less, as required in the 0.07 μm design rule. On the other hand, the EUV reflective mask 100a in Comparative Example did not satisfy the accuracy of 16 nm or less as required in the 0.07 μm design rule.

As described above, according to this invention, it is possible to provide a method of producing a glass substrate for a mask blank, which includes a polishing step of polishing a surface of the glass substrate subjected to local machining in order to repair a roughened surface resulting from the local machining and to remove a surface defect resulting from the local machining, and which is capable of providing a glass substrate high in flatness and smoothness and free from the surface defect by repairing the roughened surface of the glass substrate and removing the surface defect of the glass substrate during the polishing step while maintaining the flatness of the surface of the glass substrate. It is also possible to provide a method of producing a mask blank by the use of the above-mentioned glass substrate.

Although the present invention has been shown and described in conjunction with a few preferred embodiments or examples thereof, it will readily be understood by those skilled in the art that the present invention is not limited to the foregoing description but may be changed and modified in various other manners without departing from the spirit and scope of the present invention as set forth in the appended claims.